

Computational Materials Design for Superconductivity in Hole-Doped Delafossite CuAlO_2 : Transparent Superconductors

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Abstract

We have calculated the superconducting critical temperature T_c of hole-doped delafossite CuAlO_2 based on the first-principles calculations. According our calculation, 0.2 \sim 0.3 hole-doped CuAlO_2 can become a phonon-mediated high- T_c superconductor with $T_c \simeq 50$ K. In the hole-doped CuAlO_2 , the A_1L_1 phonon mode that stretches O-Cu-O dumbbell has a strong interaction with electrons of the flat band in Cu $3d_{3z^2-r^2}$ and the O $2p_z$ anti-bonding π -band.

Keywords: A. Semiconductors; C. Delafossite structure; D. Electron-phonon interactions; E. Density functional theory

1. Introduction

Kawazoe *et al.* have discovered the delafossite structure of CuAlO_2 is the transparent p -type conductor without any intentional doping.[1] Transparent p -type conductors such as CuAlO_2 are rare and absolutely necessary for the p - n junction of the transparent conductors and high-efficient photovoltaic solar cells. Many applications of CuAlO_2 for flat panel displays, photovoltaic solar-cells, touch panels, and high efficiency thermoelectric-power materials with about 1% hole-doping[2, 3] are expected.

Recently, Katayama-Yoshida *et al.* have suggested a new application of CuAlO_2 for transparent superconductivity and high-efficient thermoelectric-power material with a large Seebeck coefficient caused by the flat band.[4]

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They have simulated the p -type doped CuAlO_2 by shifting the Fermi level rigidly with FLAPW method, and proposed that the nesting Fermi surface may cause a strong electron-phonon interaction and a transparent superconductivity for visible light due to the large band gap ($\sim 3.0\text{eV}$). But, the calculation of superconducting critical temperature T_c is not carried out. In this study, we calculated the electron-phonon interaction and the T_c of p -type doped CuAlO_2 based on the first principles calculation with the density functional perturbation theory.[5] We found that the T_c goes up to about 50 K due to the strong electron-phonon interaction and high phonon frequency caused by the two dimensional flat band in the top of the valence band.

2. Calculation Methods

The calculations are performed within the density functional theory[6, 7] with a plane-wave pseudopotential method, as implemented in the Quantum-ESPRESSO code.[8] We employed the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) exchange-correlation functional[9] and ultra-soft pseudopotentials.[10] For the pseudopotentials, Cu 3d electrons were also included in the valence electrons. In reciprocal lattice space integral calculation, we used $8 \times 8 \times 8$ (electron and phonon) and $32 \times 32 \times 32$ (average at Fermi level) \mathbf{k} -point grids in the Monkhorst-Pack grid.[11] The energy cut-off for wave function is 40 Ry and that for charge density is 320 Ry. These \mathbf{k} -point meshes are fine enough to achieve convergence within 0.1 mRy/atom in the total energy. The $32 \times 32 \times 32$ mesh for average at Fermi level is enough to achieve convergence in the electron-phonon interaction and the superconducting critical temperature. The differences between results of $32 \times 32 \times 32$ k-points mesh and those of $64 \times 64 \times 64$ one are less than 1%.

The delafossite structure belongs to the space group $R\bar{3}m$ (No.166) and is represented by cell parameters a and c , and internal parameter z (See Fig. 1). These cell parameters and internal parameter were optimized by the constant-pressure variable-cell relaxation using the Parrinello-Rahman method[12] without any symmetry requirements. The results of relaxation ($a = 2.861\text{\AA}$, $c/a = 5.969$ and $z = 0.1101$) agree very well with the experimental data ($a = 2.858\text{\AA}$, $c/a = 5.934$ and $z = 0.1099$ [13, 14]).

In this study, some properties of hole-doped CuAlO_2 are approximated because it is difficult for first-principles calculation to deal with the doped system exactly. Let's take the electron-phonon interaction λ for example. λ is defined as follows:

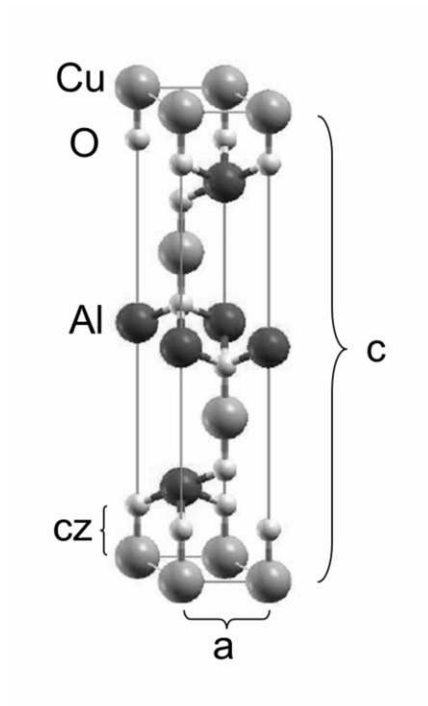


Figure 1: The crystal structure of delafossite CuAlO_2 .

$$\lambda = \sum_{\nu \mathbf{q}} \frac{2N(\varepsilon_F) \sum_{\mathbf{k}} |M_{\mathbf{k}, \mathbf{k}+\mathbf{q}}^{\nu \mathbf{q}}|^2 \delta(\varepsilon_{\mathbf{k}} - \varepsilon_F) \delta(\varepsilon_{\mathbf{k}+\mathbf{q}} - \varepsilon_F)}{\omega_{\nu \mathbf{q}} \sum_{\mathbf{k} \mathbf{q}'} \delta(\varepsilon_{\mathbf{k}} - \varepsilon_F) \delta(\varepsilon_{\mathbf{k}+\mathbf{q}'} - \varepsilon_F)}. \quad (1)$$

(1) For the non-doped CuAlO_2 , we calculated the dynamical matrix, the phonon frequency $\omega_{\nu \mathbf{q}}$ and the electron-phonon matrix $M_{\mathbf{k}, \mathbf{k}+\mathbf{q}}^{\nu \mathbf{q}}$. (2) For the doped CuAlO_2 , we calculated the Fermi level ε_F and the density of states at the Fermi level $N(\varepsilon_F)$ with the number of valence electrons reduced using the eigenvalues $\varepsilon_{\mathbf{k}}$ of the non-doped system. (3) By using the results of (1) and (2), we calculated the electron-phonon interaction λ and the other superconducting properties. This approximation is based on the rigid band model and the idea that the doping does not greatly change the phonon band structures. In this study, we show the results of $0.1 \sim 1.0$ hole-doped CuAlO_2 .

3. Calculation Results and Discussion

Before the discussion of the superconducting critical temperature, let us see the electronic structure. Fig. 2 and Fig. 3 show the electronic band structure and density of states (DOS) of non-doped CuAlO_2 . The top of the valence band of CuAlO_2 is flat due to the two dimensionality in O-Cu-O dumbbell array, and has a small peak in the DOS of the valence band. This peak is mainly constructed by the two-dimensional π -band of Cu $3d_{3z^2-r^2}$ -O $2p_z$ anti-bonding state.

Fig. 4 shows the DOS at the Fermi level calculated with the number of valence electron reduced. According to this figure and Fig. 3, the number of holes $N_h = 0.3$ corresponds to that Fermi level which is located at the top of the peak in the DOS, and $N_h = 0.9$ corresponds to that Fermi level which is located at the bottom of the DOS.

We calculated the superconducting critical temperature by using the Allen-Dynes modified McMillan's formula.[15, 16] According to this formula, T_c is given by three parameters: the electron-phonon interaction λ , the logarithmic averaged phonon frequency ω_{\log} , and the screened Coulomb interaction μ^* , in the following form.

$$T_c = \frac{\omega_{\log}}{1.2} \exp \left(-\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right). \quad (2)$$

$$\omega_{\log} = \exp \left(\frac{2}{\lambda} \int_0^\infty d\omega \frac{\alpha^2 F(\omega)}{\omega} \log \omega \right), \quad (3)$$

Here, $\alpha^2 F(\omega)$ is the Eliashberg function. λ and ω_{\log} are obtained by the first-principle calculations using the density functional perturbation theory. As for μ^* , we assume the value $\mu^* = 0.1$. This value holds for weakly correlated materials due to the electronic structure of lightly hole-doped Cu^+ (d^{10}).

The calculated result of T_c and λ as a function of N_h is shown in Fig. 5. In our calculation, the lightly doped CuAlO_2 ($N_h = 0.2 \sim 0.3$) has $T_c \simeq 50$ K. This T_c is the highest among phonon-mediated superconductors. In addition, the T_c can be increased by other purely attractive electron-electron interaction mechanisms: for example, charge-excitation-induced[17] or exchange-correlation-induced[18] negative effective U system in the Cu^+ (d^{10}) electronic structure with lightly hole-doping. The heavily doped CuAlO_2 ($N_h = 0.6 \sim 1.0$) has $T_c \simeq 10$ K by reducing the electron-phonon interaction.

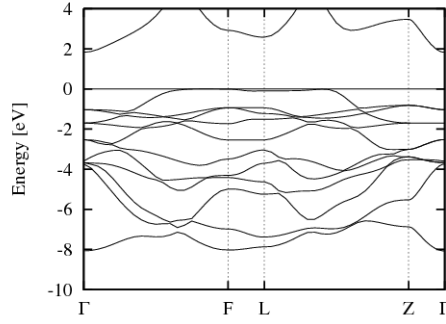


Figure 2: Band structure of CuAlO_2 .

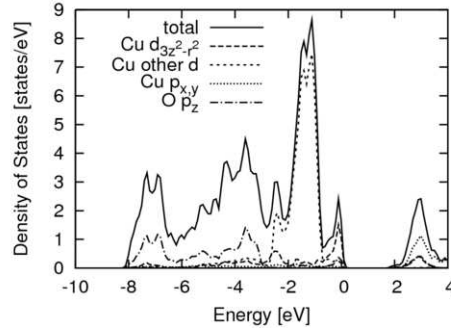


Figure 3: Total density of states(DOS) and projected DOS.

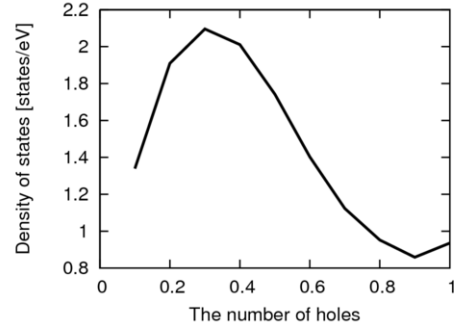


Figure 4: The number of holes vs density of states at the Fermi level.

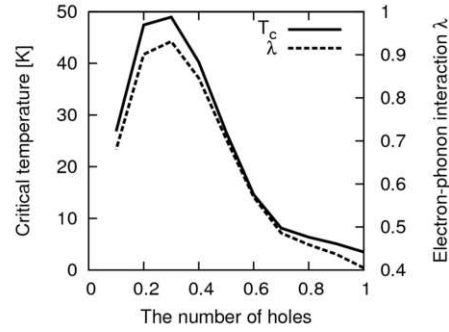


Figure 5: Superconducting critical temperature and electron-phonon interaction λ .

N_h	λ	$\omega_{\log}[K]$
0.3	0.931	789
1.0	0.405	778

Table 1: Electron-phonon interaction λ and logarithmic averaged phonon frequencies ω_{\log} . T_c has max. and min. at $N_h = 0.3, 1.0$.

Let us examine the origin of the high T_c of lightly hole-doped CuAlO_2 . In this study, the critical temperature is determined by λ and ω_{\log} as mentioned above. Table 3 shows λ and ω_{\log} . The electron-phonon interaction λ at $N_h = 0.3$ is about 130% larger than that at $N_h = 1.0$, while ω_{\log} at $N_h = 0.3$ is about 1% larger than that at $N_h = 1.0$. In addition, λ affects T_c exponentially, while ω_{\log} affects T_c linearly. Therefore, the high T_c is attributed to the strong electron-phonon interaction.

In Fig. 6, we show the phonon dispersion which show the strong two dimensionality with flat phonon dispersion. In order to find that which phonon mode has a large contribution to the high T_c , we introduce a partial electron-phonon interaction $\lambda_{\nu\mathbf{q}}$: the interaction of a phonon whose frequency is $\omega_{\nu\mathbf{q}}$. Then, $\lambda = \sum_{\nu\mathbf{q}} \lambda_{\nu\mathbf{q}}$. In Fig. 6, the $\lambda_{\nu\mathbf{q}}$ is shown by the radius of a circle on each phonon dispersion. Since most of $\lambda_{\nu\mathbf{q}}$ are very small, their circles are no longer invisible in the figure 6. This figure indicates that the highest mode on the $Z - \Gamma$ line has a large electron-phonon interaction. In the case of $N_h = 0.3$, the sum of $\lambda_{\nu\mathbf{q}}$ of the highest frequency mode is 0.407. This value is about 44% of total electron-phonon interaction $\lambda = 0.931$. The effective mode is the A_1L_1 phonon mode. In this mode, the O atoms oscillate in the anti-phase within an O-Cu-O dumbbell.

As mentioned above, the CuAlO_2 has the Cu $3d_{3z^2-r^2}$ and the O $2p_z$ electrons at the top of the valence band. When $N_h = 0.2 \sim 0.3$, the electrons which make the O-Cu-O anti-bonding band are located at the Fermi level. They have a strong interaction with the A_1L_1 phonon mode because their bonding direction is parallel to the oscillation direction of the A_1L_1 phonon mode. Though the strong electron-phonon interaction, the O-Cu-O bonding of the delafossite structure is stable even under high pressure.[19] There is a strong possibility that the doped CuAlO_2 is stable and a superconductor. When CuAlO_2 is heavily hole-doped, the total electron-phonon interaction decreases because the number of electrons which have a strong interaction decreases.

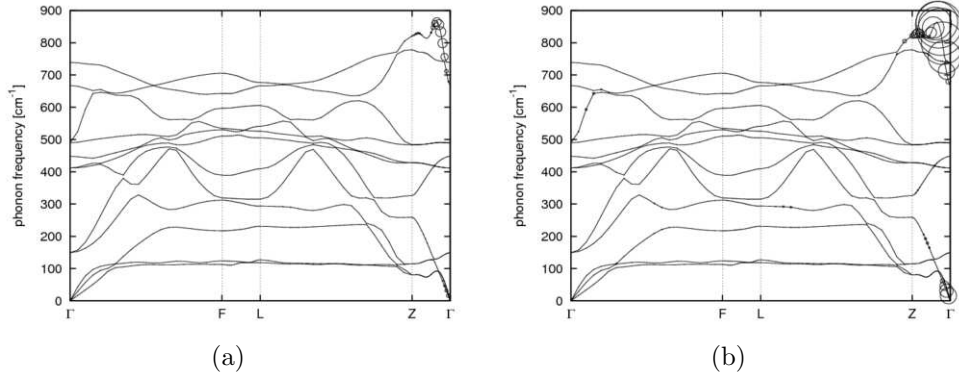


Figure 6: Phonon dispersions and electron-phonon interactions of hole-doped CuAlO_2 . The radius of circle represents the strength of partial electron-phonon interaction $\lambda_{\nu\mathbf{q}}$. Note that many $\lambda_{\nu\mathbf{q}}$ are very small and their circles are no longer invisible. (a) The number of holes $N_h = 1.0$. (b) $N_h = 0.3$.

The top of valence band is constructed by the Cu $3d_{3z^2-r^2}$ and the O $2p_z$ anti-bonding π -band.[19, 20, 21] The hole-doping makes the O-Cu-O coupling more strong. Therefore, when the density of holes increases from 0.2 to 0.3, λ and ω_{\log} does not change much ($\lambda = 0.901 \rightarrow 0.931, \omega_{\log} = 808 \rightarrow 789\text{K}$).

D. Huang and Y. Pan have investigated the intrinsic defects in CuAlO_2 . [22] According to their study, vacancies at the Cu sites and substitutional Cu at the Al site are most likely responsible for the p -type conductivity, and the transition levels of these defects are deep. The rigid-band doping is possibly not realized in CuAlO_2 . Many theoretical proposals for superconductivity-in-semiconductors (for example, LiBC[23]) are based on rigid band or other oversimplified models and not successful in experiment because doping concentrations cannot be realized or large doping levels cause material distortions not accounted for by these models. Therefore, the calculated $T_c \simeq 50\text{ K}$ may not be realized in experiment. However, we believe our calculation results suggest the superconductivity potential of hole-doped CuAlO_2 .

4. Conclusions

In summary, we calculated the superconducting critical temperature of the hole-doped delafossite CuAlO_2 by shifting the Fermi level rigidly based on the first principles calculation. The lightly hole-doped CuAlO_2 has Cu $3d_{3z^2-r^2}$ and O $2p_z$ anti-bonding π -band as the top of the valence band.

The electrons of this band have a strong electron-phonon interaction with the A_1L_1 phonon mode because the direction of O-Cu-O dumbbell is parallel to the oscillation direction of the A_1L_1 phonon mode. These findings suggest that hole-doped CuAlO_2 may be a superconductor. We hope that our computational materials design of superconductivity will be verified by experiments very soon. We can easily extend the present computational materials design to other delafossite structures of lightly hole-doped AgAlO_2 and AuAlO_2 which may have higher T_c due to the strong electron-phonon interaction combined with the charge excitation-induced[17] and exchange-correlation-induced[18] negative effective U ; such as $2\text{Ag}^{2+} (d^9) \rightarrow \text{Ag}^+ (d^{10}) + \text{Ag}^{3+} (d^8)$ and $2\text{Au}^{2+} (d^9) \rightarrow \text{Au}^+ (d^{10}) + \text{Au}^{3+} (d^8)$ [24] upon the hole-doping.

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